

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 312 702 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
21.05.2003 Bulletin 2003/21

(51) Int Cl.7: **D01F 6/62**, D06M 13/144,
D06M 13/203, D06M 15/53

(21) Application number: **02025520.4**

(22) Date of filing: **13.11.2002**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **14.11.2001 JP 2001348141**

(71) Applicant: **KURARAY CO., LTD.**
Kurashiki-City Okayama Prefecture 710 (JP)

(72) Inventors:
• **Yotsutsuji, Susumu**
Osaka-City, Osaka-Pref. (JP)
• **Andou, Yoshiyuki**
Kurashiki-City, Okayama-Pref. (JP)
• **Hokimoto, Akihiro**
Kurashiki-City, Okayama-Pref. (JP)

(74) Representative: **VOSSIUS & PARTNER**
Siebertstrasse 4
81675 München (DE)

(54) **Biodegradable fibers and fabrics, and method for controlling their biodegradability**

(57) Provided are biodegradable fibers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000, which are so designed that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and the surface

of each fiber has from 5 to 50 cracks/10 cm. The physical properties of the fibers are good and enough for practical use, and the biodegradation thereof is well controllable in any desired manner.

EP 1 312 702 A1

Description

5 [0001] The present invention relates to biodegradable fibers. More precisely, the invention relates to biodegradable fibers of polylactic acid that are expected to give biodegradable plastics ecological to the global environment and of which the biodegradation rate is controllable in accordance with their use.

[0002] Polylactic acid is one of recyclable plastics specifically noticed these days as natural resources that are ecological to the global environment. Polylactic acid fibers made from polylactic acid are expected to be popularized as biodegradable fibers that are ecological to the environment.

10 [0003] For popularizing them, biodegradable fibers must satisfy the requirement that their mechanical strength retention is at least on the same level as that of ordinary fibers such as polyester fibers in general use. Specifically, biodegradable fibers are of no service if they are not protected from being biodegraded while in ordinary use. Accordingly, various proposals have heretofore been made relating to the production and the physical properties of biodegradable fibers acceptable in practical use.

15 [0004] For example, one method proposed for efficiently producing polylactic acid fibers having stable physical properties comprises melt-spinning polylactic acid fibers, in which the melt-spun fibers are once cooled and solidified, then re-heated and exposed to air resistance applied thereto, and thereafter taken out. They say that the method promotes the orientation and the crystallization of the fiber-forming polymer used therein and gives fibers having the advantages of high mechanical strength and elasticity which could not be given by any ordinary high-speed fiber-spinning and drawing method (for example, see patent publication 1 mentioned below).

20 [0005] In another method proposed for producing polylactic acid fibers, specifically used is a hydrolysis-resistant polymer having a reduced low-molecular compound content for stabilizing the fibers in the natural environment, especially in water or under humidification (for example, see patent publications 2 and 3).

25 [0006] These proposals are for retarding the biodegradation of the fibers while in use, but they take nothing into consideration relating to a technical idea of promoting the biodegradation of the fibers after use and for controlling or retarding the biodegradation rate of the fibers really while in use. In addition, the biodegradability of the fibers and their nonwoven fabrics having such stabilized physical properties is on the level that they may lose their strength in a period of from a half year to one year after they are buried in the ground. This means that the fibrous wastes of the type require a long period of year-based time until those buried in the ground are biodegraded, and they are unsuitable to land reclamation. On the other hand, incinerating them is unfavorable from the viewpoint of preventing global warming.

30 [0007] The comparative examples to the biodegradation-retarding methods shown in the patent publications may be some examples of a biodegradation-promoting method, but they are far from a technical idea of biodegradability control which is for ensuring the stability of biodegradable fibers while in use and for rapidly biodegrading the used fibers after their disposal.

35 [0008] A method of promoting and controlling the biodegradation of articles has been investigated (for example, see patent publication 4). The method comprises adding from 10 to 40 % by weight of dry coconut powder to a polymer followed by shaping the mixture into articles. When the articles thus produced in the method are buried in the ground after their use, the dry coconut powder therein absorbs water in the ground and the buried articles are thereby swollen and biodegraded. To that effect, the method is unique in point of biodegradation control of the buried articles. In this, however, the coconut powder to be mixed with the polymer is large, having a size of from 20 to 80 μm . Therefore, the method is not applicable to fibers having a diameter of only from 14 to 30 μm .

40 [0009] Fibers having a core-sheath structure of polymers of different biodegradability or having a notched surface configuration of such different polymers have been proposed (for example, see patent publications 5 and 6). These are so designed that the polymer of lower biodegradability supports the other polymer of higher biodegradability therein to thereby prevent the fibers from being deteriorated while in use. In these, however, the biodegradation of the polymer of higher biodegradability varies, depending on the condition of the surroundings around them, and therefore, the biodegradation of the fibers themselves shall vary depending on the condition of the surroundings around them, or that is, it could not be controlled irrespective of the condition of the surroundings around the fibers. Accordingly, the life of the products made of the fibers varies depending on the surroundings in which they are used, and the biodegradation of the fibrous products is not promoted at all when the used products are disposed of. In other words, the method proposed is not for controlling the biodegradation of the fibers.

50 [0010] Similarly to the present invention, a method of notching the surfaces of fibers has been proposed, for example, as follows:

55 [0011] The method proposed comprises thermally stretching fibers to a draw ratio not lower than the maximum draw ratio thereof to thereby form uniform voids inside the fibers, and the surfaces of the fibers thus stretched therein shall have streaky notches (see patent publication 7). However, the fibers take a long time of 18 months before they are actually biodegraded, as in the examples given in the patent publication, and their biodegradability control does not meet the actual practice of processing and biodegrading used fibers.

[0012] Biodegradable fibers that are most preferred in practical use are those that keep their strength while in actual

use in daily life and can be rapidly degraded after used and disposed of, or that is, those of which the biodegradability is controllable. Up to the present, however, no one has proposed such a technical idea of biodegradation control and biodegradable fibers based on that technical idea.

[0013] Patent publication 1: JP-A-11-131323 (paragraph number [0016] and Fig. 1)

[0014] Patent publication 2: JP-A-7-316272 (paragraph number [0002], lines 1 to 5 from below, and paragraph number [0005])

[0015] Patent publication 3: JP-A-9-21018 (paragraph numbers [0006] and [0007])

[0016] Patent publication 4: JP-A-9-263700 (paragraph number [0011])

[0017] Patent publication 5: JP-A-9-78427 (paragraph number [0014])

[0018] Patent publication 6: Japanese Patent No. 3,304,237 (paragraph number [0006])

[0019] Patent publication 7: JP-A-11-293519 (paragraph number [0013] and photographs that are substitutes for drawings)

[0020] A subject matter of the present invention is to solve the problems noted above and is to provide biodegradable fibers of which the physical properties are enough for practical use and of which the time of biodegradation is controllable in any desired manner.

[0021] According to the present invention it has been found that, when fibers are specifically designed to have a specific structure or when a fiber-processing agent is applied to the fibers, then the biodegradation of the fibers is retarded or promoted. Specifically, the fibers have specific cracks formed in their surfaces, and their strength is enough for ordinary practical use. On the other hand, when used articles of the fibers are disposed of or formed into compost, the fibers are actively biodegraded after having received a specific processing agent applied thereto, and their biodegradability is thereby well controllable in any desired manner.

[0022] The invention provides biodegradable fibers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000, which are characterized in that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and the surface of each fiber has from 5 to 50 cracks/10 cm.

[0023] Preferably, a fiber-processing agent having a pH of lower than 7.8 is applied to the biodegradable fibers.

[0024] Also preferably, a fiber-processing agent (a) of which the strength reduction-promoting constant (KR value) represented by the following formula (1) is smaller than 1.2 is applied to the biodegradable fibers:

$$\text{Strength Reduction-promoting Constant (KR value)} = TA/TB \quad (1)$$

wherein TA indicates the strength of the fibers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000, the fibers being so designed that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and the surface of each fiber has from 5 to 50 cracks/10 cm, and the strength thereof is measured after the fibers are degreased and then left at a temperature of 50°C and a humidity of 65 % for 7 days; and TB indicates the strength of the fibers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000, the fibers being so designed that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and the surface of each fiber has from 5 to 50 cracks/10 cm, and the strength thereof is measured after the fibers are degreased, then from 1 to 5 % by weight of the fiber-processing agent (a) is applied to the fibers under a tension of from 0.05 to 0.20 g/dtex, and the thus-processed fibers are left at a temperature of 50°C and a humidity of 65 % for 7 days.

[0025] The invention also provides a biodegradability-controlling method for promoting the biodegradation of the biodegradable fibers, which comprises processing the surfaces of the fibers with an alkaline fiber-processing agent having a pH of not lower than 7.8.

[0026] Preferably in the biodegradability-controlling method, a fiber-processing agent (b) of which the strength reduction-promoting constant (KR value) represented by the following formula (1) is not smaller than 1.2 is applied to the biodegradable fibers for promoting the biodegradation of the fibers:

$$\text{Strength Reduction-promoting Constant (KR value)} = TA/TB \quad (1)$$

wherein TA indicates the strength of the fibers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000, the fibers being so designed that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and the surface of each fiber has from 5 to 50 cracks/10 cm, and the strength thereof is measured after the fibers are degreased and then left at a temperature of 50°C and a humidity of 65 % for 7 days; and TB indicates the strength of the fibers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000, the fibers being so designed that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and the surface of each fiber has from 5 to 50 cracks/10 cm, and the strength

thereof is measured after the fibers are degreased, then from 1 to 5 % by weight of the fiber-processing agent (b) is applied to the fibers under a tension of from 0.05 to 0.20 g/dtex, and the thus-processed fibers are left at a temperature of 50°C and a humidity of 65 % for 7 days.

[0027] Also preferably in the biodegradability-controlling method, a processing agent that contains at least 1 % by weight of at least one component selected from a group consisting of polyoxyethylene phosphates, phosphate salts, phosphate amines and oleic acids is applied to the biodegradable fibers for promoting the biodegradation of the fibers.

[0028] The invention also provides a fabric formed of the biodegradable fibers.

[0029] Fig. 1 is a photograph (substitute for drawing) that shows a cross section of the fiber morphology of the biodegradable fibers of the invention before processed with an alkaline solution.

[0030] Fig. 2 is a photograph (substitute for drawing) that shows a cross section of the fiber morphology of the biodegradable fibers of the invention after processed with an alkaline solution.

[0031] Fig. 3 is a side-view photograph (substitute for drawing) of the biodegradable fibers of the invention.

[0032] Fig. 4 is a side-view photograph (substitute for drawing) of conventional biodegradable fibers.

[0033] The invention is described in detail hereinafter.

[0034] It is a matter of importance that the polylactic acid for use in the biodegradable fibers of the invention uses a polymer having a number-average molecular weight of from 50,000 to 150,000. Polylactic acid having a number-average molecular weight of smaller than 50,000 is unfavorable to the invention, as the strength of its fibers is not enough for practical use. In addition, the surfaces of the fibers formed of it could not be favorably cracked when having received external force in drawing, crimping or false-twisting them. As opposed to it, polylactic acid having a number-average molecular weight of larger than 150,000 could not be well spun into fibers since its flowability is poor. This is because the melt viscosity of such polylactic acid polymer having a number-average molecular weight of larger than 150,000 is high, and when the polymer is run through spinning ducts, it must be heated at a high temperature of \pm melting point thereof + 80°C. If not, its pressure loss increases and the polymer could not flow through the ducts. However, when the polymer, polylactic acid is heated at such a high temperature, it greatly pyrolyzes to give oligomers, and the resulting oligomers soil spinning nozzles and cause various spinning troubles. For example, the fibers of the polymer being spun are often cut and are much fluffed. For these reasons, the polymer, polylactic acid having a number-average molecular weight of larger than 150,000 is unfavorable to the invention. From the viewpoint of the physical properties and the spinnability of the fibers of the polymer, the number-average molecular weight of the polylactic acid for the fibers preferably falls between 60,000 and 120,000, more preferably between 70,000 and 110,000.

[0035] The polylactic acid for use in the invention consists essentially of a copolymer of optical isomers of L-lactic acid and D-lactic acid, of which, poly-L-lactic acid is generally used in the art.

[0036] Preferably, poly-L-lactic acid for use in the invention has an optical purity of from 90.0 to 99.5 %. Increasing the content of the other optical isomer, D-lactic acid in the polymer may lower the crystallinity and the melting point of the polymer, therefore often detracting from the heat resistance of the fibers of the polymer. On the other hand, however, too much decreasing the D-lactic acid content of the polymer may detract from the biodegradability of the fibers of the polymer. In general, fibers for ordinary use must be resistant to heat. For these, therefore, it is more desirable that the optical purity of the poly-L-lactic acid falls between 96.0 and 99.5 %. Binder fibers must have a low melting point, for which, therefore, it is more desirable that the optical purity of the polymer falls between 90.0 and 96.0 %.

[0037] Not interfering with the advantages of the invention, any other resin and additive may be added to the polymer.

[0038] The fibers of the invention must have a fiber structure of such that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof. Briefly, the fiber structure of the fibers of the invention is so designed that its outer part (surface part) is resistant to hydrolysis but the inside part (nearer to the center part) thereof is not resistant to hydrolysis.

[0039] In the polylactic acid fibers of the invention, it is desirable that the polymer having a large molecular weight is first hydrolyzed to a size capable of being degraded with enzyme, and then biodegraded with enzyme. This means that fibers resistant to hydrolysis as a whole are hardly biodegraded and therefore could not have the advantage of biodegradation control of the invention. In addition, the fibers of the type are unsuitable to the biodegradability-controlling method of the invention described below in which the inside part of each fiber is first hydrolyzed to initiate the fiber biodegradation. For promoting hydrolysis of fibers, a method may be taken into consideration of exposing fibers to a high-temperature and high-humidity environment or spraying them with a strong alkaline solution. However, the method of exposing fibers to a high-temperature and high-humidity environment is unfavorable for ecological treatment of used fibrous products for the following reasons: The method requires some troublesome work of collecting the used products; transporting the thus-collected used products gives a negative load to the environment; and exposing them to high temperature and high humidity also gives a negative load to the environment. The other method of spraying strong alkali on used fibrous products will be effective for promoting fiber hydrolysis, but is unfavorable for the following reasons: Strong alkali enough to promote fiber hydrolysis with it kills biodegrading enzyme that is not resistant to alkali, and therefore retards the biodegradation of the fibrous products sprayed with it, and, in addition, it further increases a negative load given by it to the environment.

[0040] Contrary to the above, if the biodegradability of fibers is too high as a whole, the strength of the fibers will lower while in use and the fibers are unacceptable for practical use. Therefore, the fibers of the type are also unfavorable.

[0041] In order that the biodegradable fibers satisfy the requirement of the invention that the fibers keep their strength while in use and, after used to be disposed of, their biodegradation is promoted, it is a matter of importance that the fibers are so designed that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof.

[0042] In addition, it is another matter of importance that the biodegradable fibers of the invention have cracks in their surfaces. Cracks in their surfaces make it possible to control the biodegradability of the fibers, or that is, to control the biodegradation rate of the fibers while the strength of the fibers is enough for practical use. In the surfaces of the fibers, cracks may run in various directions including the direction of the fiber axis and the direction perpendicular to the fiber axis. Of the cracks, those running in the direction perpendicular to the fiber axis preferably have a mean length of from 1/40 to 2/3 of the outer periphery that surrounds the cross section of each fiber. If the mean length of the cracks is larger than 2/3 of the outer periphery, the fiber strength will be low and the fibers having such long cracks will be unsuitable to practical use if the long cracks are too deep. The cracks running in the direction of the fiber axis may have different lengths. Preferably, their lengths fall between 1/20 and 3 times the fiber diameter in order that the fibers may have the necessary strength. Also preferably, the depth of each crack running inside the fibers falls between 3 and 30 % of the fiber diameter. If the crack depth is smaller than 3 % of the fiber diameter, the fiber-processing agent applied to the fibers could hardly penetrate into the depth of each fiber of high alkali solubility, and the biodegradability of the fibers could not be well controlled. On the contrary, if the crack depth is larger than 30 % of the fiber diameter, the strength of the fibers will be low and the fibers having such deep cracks will be unsuitable to practical use if the deep cracks are too long.

[0043] The cracks serve as capillaries through which a fiber-processing agent is led into the fibers. The fiber-processing agent assists the propagation of biodegrading enzyme in the fibers to thereby promote the biodegradation of the fibers, and this will be described hereinafter. The fibers having such cracks of the invention basically differ from other fibers of which the surfaces are notched so as to make the fibers have a dry feel, in point of both the structure and the object thereof. Another advantage of the invention is that the biodegradation of the fibers may be promoted or retarded in accordance with the intended object of the fibers, depending on the type of the processing agent applied to the fibers.

[0044] It is still another matter of importance that the surface of each fiber of the invention has from 5 to 50 cracks/10 cm. Preferably, the fiber surface has from 8 to 40 cracks/10 cm, more preferably from 10 to 30 cracks/10 cm. If the number of the cracks in the fiber surface is smaller than 5 per 10 cm, the biodegradation of the fibers could not be well promoted even when the fibers are processed with a fiber-processing agent. On the other hand, if the number of the cracks in the fiber surface is larger than 50 per 10 cm, the fiber strength will be low or the fibers will become weak while in use, and the fibers are therefore unsuitable to practical use. The number of cracks in the fiber surface may be counted by observing the fibers with a scanning electronic microscope (SEM).

[0045] The structure of the cross section of the fibers of the invention, which are so designed that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof, is seen in the photographs of Fig. 1 and Fig. 2. The fibers in the photograph of Fig. 1 are those before processed for alkali dissolution; and the fibers in the photograph of Fig. 2 are those after processed with an aqueous 1 N alkali solution at 50°C for 15 minutes for dissolution and hydrolysis. As in Fig. 2, it is seen that the outer skin of each fiber (outside of each fiber) remains while the inside thereof (inner part of each fiber) is corroded. This will be because the fibers are so designed that the alkali solubility of the outer peripheral part in the cross section of each fiber is low while that of the inside part, or that is, the inner part of thereof is high. We, the present inventors define such a fiber structure that gives the cross-section structure morphology as in Fig. 2 through the alkali dissolution treatment as above, as the fiber structure of which the inside part alkali dissolution is higher than the outer peripheral part alkali dissolution thereof.

[0046] Depending on the alkali dissolution treatment, a cross section of a fiber of which the shell is partly dissolved, or a cross section of a fiber of which the inside part is slowly decomposed and dissolved to have a porous structure may be seen. This will be because the polylactic acid polymer to form the fibers is extremely rapidly hydrolyzed with alkali and is therefore difficult to uniformly dissolve, and because the fibers dissolve in alkali at different rates.

[0047] In view of the above, according to the present invention the fibers of the invention of which the inside part alkali dissolution is higher than the outer peripheral part alkali

dissolution thereof, are defined as follows: When fibers to form filaments are dissolved in alkali and when the number of the thus-dissolved fibers each having from 10 % to 95 % of voids formed inside them is at least 50 % of the total number of the filaments, then according to the present invention the fibers of the type are defined

as the fibers of which the inside part alkali dissolution is higher than the outer peripheral part alkali dissolution thereof.

[0048] Preferably, the shell of the cross section of each fiber of the invention of which the inside part alkali dissolution is higher than the outer peripheral part alkali dissolution thereof (the outer periphery and therearound of the cross

section of each fiber of which the alkali dissolution is low) has a thickness of from 5 to 20 % of the mean diameter of the fibers, more preferably from 10 to 20 % thereof. If the shell thickness is smaller than 5 % of the mean diameter of the fibers, the strength of the fibers will time-dependently lower even though they are not subjected to biodegradation-promoting treatment. On the other hand, if it is larger than 20 %, a processing agent could not well penetrate into the inside area of the fibers even though their surfaces have cracks, and, as a result, the fibers of the type could not be well biodegraded.

[0049] If the fibers of the invention are processed with an aqueous alkali solution of higher concentration at higher temperatures and for a longer period of time than the above, the fibers will be entirely dissolved, and if so, no one could confirm the specific fiber structure of the invention that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof. Therefore, in this respect, special attention should be paid to the condition of the alkali dissolution treatment of the fibers of the invention.

[0050] For expressing the fiber structure of such that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and that each fiber surface has cracks, a rigid polymer having a number-average molecular weight of at least 50,000 must be used in forming the fibers. Preferably, the draw ratio of the spun fibers is defined high to fall between 85 % and 120 % of the elongation at break of the fibers measured at room temperature (25°C). If the draw ratio thereof is smaller than 85 %, the fibers could not have the intended fiber structure of such that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof, and, in addition, voids will be difficult to form inside each fiber. If so, therefore, the fibers could not have cracks in their surfaces. On the other hand, if the draw ratio of the fibers is larger than 120%, too many voids will be formed inside each fiber, and the fibers will be too much fluffed and will be often cut during their formation. As a result, the productivity of the fibers will lower and, in addition, the fiber strength will be low.

[0051] In this connection, ordinary polyester fibers will be much fluffed and will often cut, when drawn to a draw ratio of at least 85 % of the elongation at break thereof, and their productivity will be low. As opposed to these, however, the polylactic acid fibers of the invention hardly cut even through they are drawn to the high draw ratio as above.

[0052] According to the present invention it has been found that the draw ratio of polylactic acid fibers to the elongation at break thereof greatly varies, depending on the temperature of the atmosphere in which they are drawn (in case of dry heat drawing, this is the temperature of the heating roller used for drawing the fibers). Experiments show that the draw ratio to the elongation at break of high-speed spun raw fibers of polylactic acid (hereinafter referred to as POY raw fibers) that are wound up at a winding speed of 3000 m/min at a temperature of 110°C of the atmosphere in which the fibers are drawn is 1.15 relative to the elongation at break thereof of 1 that are drawn at an atmosphere temperature of 60°C at the same winding speed. The draw ratio to the elongation at break of the POY raw fibers that are drawn at an atmosphere temperature of 120°C at the same winding speed greatly increases to 1.40 or more. This will be because of the following reasons: When the polymers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000 are drawn at a high atmosphere temperature to a draw ratio over the elongation at break thereof at room temperature (25°C), the surface of each fiber is highly drawn as its temperature is high but the inside thereof is hardly drawn as its temperature is lower than that of the outer surface thereof, and this produces a draw ratio difference between the inside and the outer surface of each fiber. The draw ratio difference would lead to the alkali solubility profile of the fibers of the invention of such that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof. Of the fibers drawn to the same draw ratio, those for which the temperature of the heating roller is lower shall have more strain, as will be described hereinafter, and the fibers drawn at such a higher temperature may have the specific fiber structure of such that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and may have more strain to form more cracks in their surfaces. Accordingly, the temperature of the heating roller to be used for drawing the biodegradable fibers of the invention under dry heat preferably falls between 50 and 140°C, through varying depending on the drawing rate. If the drawing temperature is lower than 50°C, it is lower than the glass transition point of the polymer to form the fibers, and the drawing mode at such a low temperature is cold drawing. Such cold drawing is unfavorable to the invention since too many cracks will be formed in the fiber surface and the fiber productivity will be low. On the other hand, however, if the drawing temperature is higher than 140°C, the fibers being drawn at such a high temperature will move and will be therefore fluffed and cut, and their productivity will be therefore low. In case where the fibers are drawn under wet heat, the temperature of the drawing bath preferably falls between 50 and 95°C. If the bath temperature is lower than 50°C, it is lower than the glass transition point of the polymer to form the fibers and the drawing mode at such a low temperature is cold drawing, like in the case of dry heat drawing. Such cold drawing is also unfavorable to the invention since too many cracks will be formed in the fiber surface and the fiber productivity will be low. The uppermost limit of the temperature in the wet heat drawing is 95°C for mass-production of the fibers since water is in the drawing bath.

[0053] A side-view photograph of the biodegradable fibers of the invention is in Fig. 3; and that of conventional biodegradable fibers is in Fig. 4. As in the photograph of Fig. 3, many cracks are seen in the side surfaces of the fibers of the invention; but no crack is seen in the side surfaces, conventional biodegradable fibers, as in the photograph of Fig. 4.

[0054] For forming the cracks, the mechanism of forming them must be taken into consideration. According to the present invention it has been found that the crack formation will be correlated to the number-average molecular weight of the polylactic acid to constitute the fibers and to the voids formed inside each fiber. In general, the specific gravity of thermoplastic fibers increases with the increase in the crystallinity thereof drawn high. Contrary to these, when the polylactic acid fibers of the invention are drawn high, they retain the drawing strain inside them and therefore have minute cavities, so-called voids inside them. Studies revealed that the specific gravity of the drawn fibers is not larger than 0.95 relative to that of the non-drawn raw fibers of 1, and this suggests the formation of voids inside the drawn fibers. Thus formed, the voids are cleaved by external force applied thereto, and they give cracks. Concretely, the voids formed in short fibers are cleaved by external force applied thereto, for example, in a forced crimping step or in a spinning step, and they give cracks; while those formed in long fibers are cleaved by external force applied thereto, for example, in a false-twisting or pneumatically processing step, and they give cracks. Accordingly, the fibers of the invention have many cracks in the bent parts thereof in which the external force applied thereto concentrates.

[0055] Regarding the crimping condition in forming cracks in the surfaces of the fibers of the invention, it is desirable that the pressure at the inlet of the crimper falls between 2.0 and 6.0 kg/cm², the pressure at the outlet thereof falls between 2.0 and 5.5 kg/cm², and the crimping rate falls between 60 and 150 m/min. More preferably, the pressure at the inlet of the crimper falls between 2.5 and 3.5 kg/cm², the pressure at the outlet thereof falls between 2.0 and 3.5 kg/cm², and the crimping rate falls between 60 and 100 m/min. If the pressure at the inlet and that at the outlet of the crimper are over 6.0 kg/cm² or 5.5 kg/cm², respectively, too many cracks will be formed and the physical properties of the fibers will be therefore not good. As the case may be, the fibers will be cut. On the other hand, if the pressure at the inlet and that at the outlet of the crimper are lower than 2.0 kg/cm², the number of cracks to be formed will reduce and the biodegradability of the fibers will be difficult to control. The preheating temperature of the fibers to be crimped preferably falls between 55 and 75°C. If the preheating temperature is lower than 55°C, the fibers will be difficult to crimp and the number of cracks to be formed will reduce. If so, the biodegradability of the fibers will be difficult to control. On the other hand, if the preheating temperature is higher than 75°C, it is unfavorable since the fibers will agglutinate to each other.

[0056] For false-twisting the fibers, a friction-type false twister is preferred to a pin-type false twister. Though depending on the type of the spinning oil used, polylactic acid fibers generally have a high friction resistance and their untwisting tension tends to increase. In pin false-twisting, the ratio of untwisting tension/twisting tension of polylactic acid fibers falls between 3 and 5, and is about 1.5 to 2.5 times that of ordinary polyester fibers. Therefore, when false-twisted in a pin-type false twister, polylactic acid fibers will be much fluffed and more than 50 cracks/10 cm will be formed in their surfaces. Also in a friction-type false twister, polylactic acid fibers will have a high untwisting tension, but it is from 1.1 to 1.3 times that of ordinary polyester fibers. In friction false-twisting, in addition, polylactic acid fibers are prevented from being too much fluffed and cracked. For these reasons, the latter friction-type false twister is preferred to the former pin-type false twister for polylactic acid fibers. Regarding the false-twisting condition for the fibers, it is desirable that the heater temperature is not higher than 160°C, and the count of false twists of the fibers falls between 2000 and 2500 twists/m in terms of the fibers of 167 dtex. More preferably, the heater temperature falls between 120 and 150°C, and the count of false twists of the fibers falls between 2200 and 2400 twists/m in terms of the fibers of 167 dtex. If the heater temperature is higher than 160°C, the fibers will agglutinate to each other and too many cracks will be formed in their surfaces, and therefore the physical properties of the fibers will be not good. On the other hand, if the heater temperature is lower than 120°C, the fibers will be poorly false-twisted and their quality will be not good. If the count of false twists of the fibers is more than 2500 twists/m, the fibers will be too much fluffed and will often cut, and their productivity will lower. If so, in addition, too many cracks are formed and the physical properties of the fibers will be not good. On the other hand, if the count of false twists of the fibers is less than 2000 twists/m, it is unfavorable since the fibers will be poorly false-twisted and the quality of the fibers will be not good. The optimum draw ratio of the fibers varies, depending on the heater temperature, and therefore could not be indiscriminately defined. In general, however, it is desirable that the draw ratio of the fibers falls between 60 and 80 % of the elongation at break thereof at room temperature. If the draw ratio of the fibers is higher than 80 % of the elongation at break thereof, too many cracks will be formed and the physical properties of the fibers will be not good. On the other hand, if the draw ratio of the fibers is lower than 60 % of the elongation at break thereof, the false-twisting tension of the fibers will be low and the fibers will often cut. As a result, the processability of the fibers in the false-twisting step will be poor. Cracks of the fibers result from the tension and the twisting force thereof while the fibers are processed in the false-twisting step, and the number of the cracks to be formed is readily controlled to fall between 5 and 50 per 10 cm so far as the tension and the twisting force of the fibers in the step do not overstep the uppermost limit thereof. Especially preferably, the false-twisting condition for the fibers is so planned that the false-twisting temperature falls between 130 and 150°C, the count of false twists of the fibers falls between 2300 and 2400 twists/m in terms of the fibers of 165 dtex, and the draw ratio of the fibers falls between 70 and 75 % of the elongation at break thereof.

[0057] A fiber-processing agent may adhere to the biodegradable fibers of the invention.

[0058] The fiber-processing agent that may adhere to the fibers is preferably so controlled that its pH is lower than

7.8 in every final step of spinning, weaving or knitting, coloring and sewing the fibers and their fabrics. More preferably, the pH of the fiber-processing agent falls between 4.0 and lower than 7.8. Having such a fiber-processing agent that has a pH of lower than 7.8 applied thereto, the biodegradability of the fibers is retarded and the strength thereof is kept high, and therefore the fibers are suitable to practical use. However, a fiber-processing agent of which the pH is not lower than 7.8 promotes the biodegradation of the fibers. Therefore, if the agent is applied to the fibers, its action on the fibers must be blocked off until the fibers, after used, are disposed of and formed into compost. The fiber-processing agent includes, for example, spinning oil and false-twist coning oil that are applied to the fibers being spun. For fabrics of the fibers, the fiber-processing agent may be any of size to be applied to them being woven, and knitting oil to be applied to them being knitted. Other examples of the fiber-processing agent are a scouring agent, a dyeing promoter, a pH-controlling agent, an antistatic agent and a sewing improver that are applied to the fibers or their products being dyed. Regarding the fiber-processing agent content of the fibers, the spinning oil content thereof is preferably at most 1.0 % by weight, and the amount of the finishing agent to be applied to the fibers or their products being dyed preferably falls between 0.3 and 0.5 % by weight though varying depending on the type and the object of the agent.

[0059] According to the present invention it has been found that the degradation of the biodegradable fibers of the invention is retarded or promoted depending on the fiber-processing agent applied to the fibers. Specifically having cracks in their surfaces, the strength of the fibers of the invention is enough for ordinary practical use, but when a processing agent, for example, an alkaline fiber-processing agent is applied to the used products of the fibers to be disposed of and to be formed into compost, then the biodegradability of the fibers is promoted, or that is, the biodegradability of the fibers is controlled before and after having received the processing agent.

[0060] Specifically, when the biodegradable fibers of the invention are processed with an alkaline fiber-processing agent having a pH of 7.8 or more before they are disposed of and are formed into compost, their biodegradation is promoted. In addition, the biodegradability of the fibers may be controlled by controlling the number of the cracks in their surfaces.

[0061] The alkaline fiber-processing agent that may be applied to the used products of the fibers to be disposed of and to be formed into compost is not specifically defined, and it may be any and every solution or processing-agent having a pH of 7.8 or more. Preferably, the processing-agent has a pH of 8.5 or more as more rapidly promoting the degradation of the fibers and their products. However, strong alkali having a pH of 10 or more will have some other negative influences on the global environment. Most preferably, therefore, the fiber-processing agent for promoting the degradation of the fibers is an alkaline fiber-processing agent having a pH of from 8.5 to less than 10. Still another advantage of the invention is that the biodegradation rate of the fibers is controllable in any desired manner by suitably controlling the pH of the processing agent to be applied to the fibers.

[0062] Preferably, a fiber-processing agent (a) of which the strength reduction-promoting constant (KR value) is smaller than 1.2 is applied to the biodegradable fibers of the invention while or after the fibers are produced or while or before they are used. One advantage of the fiber-processing agent (a) of the type to be applied to the fibers is that the fibers processed with it keeps their strength while in ordinary daily use thereof.

[0063] The strength reduction-promoting constant (KR value) of the fiber-processing agent (a) is represented by the following formula (1):

$$\text{Strength Reduction-promoting Constant (KR value)} = TA/TB \quad (1)$$

wherein TA indicates the strength of the fibers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000, the fibers being so designed that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and the surface of each fiber has from 5 to 50 cracks/10 cm, and the strength thereof is measured after the fibers are degreased and then left at a temperature of 50°C and a humidity of 65 % for 7 days; and TB indicates the strength of the fibers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000, the fibers being so designed that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and the surface of each fiber has from 5 to 50 cracks/10 cm, and the strength thereof is measured after the fibers are degreased, then from 1 to 5 % by weight of the fiber-processing agent (a) is applied to the fibers under a tension of from 0.05 to 0.20 g/dtex, and the thus-processed fibers are left at a temperature of 50°C and a humidity of 65 % for 7 days.

[0064] Degreasing the fibers may be effected in any known manner. For example, the fibers may be processed with any of polar solvents such as alcohol, or water or halogen-containing solvents, depending on the properties of the fiber-processing agent having been applied to the fibers.

[0065] The fiber-processing agent (a) applicable to the fibers includes, for example, spinning oil and false-twist coning oil that are applied to the fibers being spun. For fabrics of the fibers, the fiber-processing agent (a) may be any of size to be applied to them being woven, and knitting oil to be applied to them being knitted. Other examples of the fiber-processing agent (a) are a scouring agent, a dyeing promoter, a pH-controlling agent, an antistatic agent and a sewing

improver that are applied to the fibers or their products being dyed.

[0066] Of the fiber-processing agents (a), preferred are those of which the strength reduction-promoting constant (KR value) represented by formula (1) falls between 1 and less than 1.2.

5 **[0067]** One preferred example of the fiber-processing agent (a) that satisfies the requirement is formulated by mixing a spinning oil ([KE3400] produced by TAKEMOTO OIL & FAT Co., LTD.) having a strength reduction-promoting constant (KR value) of 1.14 and having a pH of 7.2. Other examples of the fiber-processing agent (a) for use in the invention may be formulated by mixing the necessary components in any desired ratio so that the resulting compositions satisfy the requirement of the value of formula (1) being smaller than 1.2.

10 **[0068]** Another preferred method of controlling the biodegradability of the fibers of the invention comprises applying a fiber-processing agent (b) of which the strength reduction-promoting constant (KR value) represented by formula (1) is 1.2 or more to the fibers to thereby promote the biodegradation of the fibers.

[0069] Preferred examples of the fiber-processing agent (b) for that purpose are a composition formulated by mixing a potassium stearyl phosphate, a polyether, an alkyl ether, a laurylamine and a nonionic surfactant in a ratio of 50:22:13:10:5, having a strength reduction-promoting constant (KR value) of 1.30 and having a pH of 9.5; and an oil ([TOR-ICOL M75] produced by TAKEMOTO OIL & FAT Co., LTD.), having a strength reduction-promoting constant (KR value) of 1.25 and having a pH of 6.5. Except those, also employable herein are any others prepared by mixing the necessary components in any desired ratio to have the KR value of formula (1) of 1.2 or more.

20 **[0070]** Regarding the amount of the fiber-processing agent (a) of which the strength reduction-promoting constant (KR value) is smaller than 1.2 and which may be applied to the fibers while the fibers are produced or while or before they are used, the content of the spinning oil to be in the fibers preferably falls between 0.2 % by weight and 1.0 % by weight, and the content of the finishing agent to be applied to the fibers or their products being dyed preferably falls between 0.3 and 0.5 % by weight or so though varying depending on the type and the object of the agent.

25 **[0071]** The results of the studies according to the present application have confirmed that a processing agent that contains at least 1 % by weight of at least one biodegradation-promoting component selected from a group consisting of organicphosphate salts, unsaturated fatty acids and unsaturated alcohols is preferred for promoting the biodegradation of the fibers.

30 **[0072]** For example, polyoxyethylene phosphate salts (especially preferably, C8 to C18 polyoxyethylene phosphate salts) and phosphate amines are especially preferred for promoting the reduction in the strength of the fibers. Though having a pH of lower than 7.8, also preferred are unsaturated fatty acids of C8 to C18, and especially preferred are oleic acid, and higher unsaturated alcohols of C8 to C18, and especially preferred are oleyl alcohol, as they promote the reduction in the strength of the fibers. Regarding the fiber-processing agent content of the fibers, the spinning oil content thereof preferably falls between 0.2 % by weight and 10.0 % by weight, and especially preferably falls between 0.3 and 8 % by weight though varying depending on the type and the object of the agent.

35 **[0073]** As so mentioned hereinabove, an alkaline solution such as aqueous sodium hydroxide solution having a pH of 10 or more kills microorganisms and will have some other negative influences on the global environment, and is therefore unfavorable to the invention. Even if the used fibers and their products are buried in the ground into which sugar-containing water or the like has been infiltrated for promoting the growth of microorganisms therein, their biodegradation could not be promoted.

40 **[0074]** Fig. 1 and Fig. 2 are photographs showing the fiber morphology of the biodegradable fibers of the invention before and after processed with an alkaline solution, respectively. As in these, it is seen that the fibers before processed with an alkaline solution keep their original fiber morphology even though having cracks in their surface, but after the fibers are processed with an alkaline solution, the processing agent penetrates into the center part of the cross section of each fiber through the cracks and significantly promotes the degradation of the fibers.

45 **[0075]** Regarding the effect of promoting the biodegradability of the biodegradable fibers of the invention, the strength retention of the fibers is preferably at most 50 % after the fibers are left in the ground for 4 weeks, and it may be suitably determined depending on the number of the cracks formed in the surfaces of the fibers and on the type and the amount of the processing agent to be applied to the fibers.

50 **[0076]** It is desirable that the fiber-processing agent (b) which promotes the biodegradation of the fibers and which has a strength reduction-promoting constant (KR value) of 1.2 or more is applied to the fibers or their products under high tension as much as possible, preferably under a tension of at least 1 g/cm², more preferably at least 5 g/cm², even more preferably at least 15 g/cm². Also preferably, the amount of the fiber-processing agent (b) to be applied to the fibers or their products under such high tension falls between 1 and 20 % by weight, more preferably between 3 and 12 % by weight of the fibers or their products. If its amount is smaller than 1 % by weight, the biodegradation-promoting fiber-processing agent will be ineffective. If larger than 20 % by weight, it is unfavorable since too much fiber-processing agents will pollute the global environment and will increase the cost in treating the used fibers. The test results of the studies according to the present application in which 10 % by weight of a fiber-processing agent (b) having a strength reduction-promoting constant (KR value) of 1.25 was applied to the fibers of the invention having 10 cracks/10 cm in their surfaces, under a low tension of 0.01 g/dtex, and 3 % by weight of the same fiber-processing agent

agent (b) was applied to the same fibers under a high tension of 0.15 g/dtex, have confirmed that the reduction in the strength of the fibers processed with the smaller amount of the agent under higher tension is large. This will be because the cracks in the surfaces of the fibers processed with the agent under higher tension will be broadened to facilitate the penetration of the agent into the depths of each fiber, and the test results demonstrate and support the system and the effect of the invention.

[0077] The strength of the biodegradable fibers and fabrics of the fibers is on a level with that of ordinary fibers, and they have many applications, for example, for construction materials in agriculture and those in civil engineering. After disposed of, the biodegradable fibers of the invention may be biodegraded even though no processing agent is applied thereto. However, when a processing agent is applied thereto, the biodegradation of the fibers is remarkably promoted and is well controlled. After processed with a processing agent, the fibers may be completely degraded within a few months, and they are ecological to the global environment.

EXAMPLES

[0078] The invention is described in detail with reference to the following Examples, which, however, are not intended to restrict the scope of the invention. The physical properties of the samples produced in the Examples are measured according to the methods mentioned below.

1. Specific Gravity:

A density gradient solution of a sample in a mixed solvent of n-hexane/carbon tetrachloride is put into a density gradient tube (produced by Shibayama Scientific Co., LTD), and after kept therein for 24 hours, the specific gravity of the sample is measured at 25°C +/- 0.1°C.

2. Strength, Elongation:

Measured according to JIS L1013.

3. Number of Cracks:

An enlarged photograph of fibers is taken through a scanning electronic microscope (SEM), and the number of the cracks seen in the surface of each fiber in the photograph is counted.

When exposed to electronic radiations for 20 seconds or longer, polylactic acid fibers tend to crack in their surfaces. Therefore, the measurement according to the method must be carried out rapidly.

Example 1:

[0079] A polymer poly-L-lactic acid of 6200 D grade (from Cargil-Dow LLC, having a number-average molecular weight of 78200 and an optical purity of 98.7 %) was spun into non-stretched polylactic acid fibers of 4500 dtex/704 f. The spinning head temperature was 240°C, the winding-up rate was 800 m/min, and 0.2 % by weight of spinning oil ([KE3400] produced by TAKEMOTO OIL & FAT Co., LTD,) having a strength reduction-promoting constant (KR value) of 1.14 and having a pH of 7.2 was applied to the fibers being spun. The specific gravity of the non-stretched fibers was 1.3105, and the elongation at break thereof was 330 %.

[0080] The non-stretched fibers were bundled up into non-stretched tow of 516,000 dtex. The tow was then drawn in two stages. Concretely, the water bath temperature in the first drawing stage was 70°C, the water bath temperature in the second drawing stage was 95°C, the draw ratio in the first drawing stage was 3.50 times, the draw ratio in the second drawing stage was 1.23 times, and the total draw ratio was 4.30 times (100 % of the elongation at break). 0.3 % by weight of [KE3400] (produced by TAKEMOTO OIL & FAT Co., LTD,) having a strength reduction-promoting constant (KR value) of 1.14 and having a pH of 7.2 was applied to the stretched tow, which was then crimped. For this, the forced crimper used had an inlet pressure of 3.0 kg/cm² and an outlet pressure of 2.5 kg/cm² and crimping rate was 80 m/min. Thus crimped, the number of buckles of the tow was 14 or 15 per 2.5 cm. The thus-crimped tow was cut with a cutter into 38-mm pieces, polylactic acid short fibers having a single fiber fineness of 1.5 dtex. The number of the cracks formed in the surfaces of the stretched short fibers was 48 per 10 cm of each single fiber, the specific gravity of the short fibers was 1.2323, the strength at break thereof was 3.1 cN/dtex, and the elongation at break thereof was 30.5 %. In point of their strength and elongation, the short fibers have no problem in practical use thereof.

[0081] The short fibers were spun in an ordinary manner into yarn of 10 tex.

[0082] The spun yarn was woven into victoria lawn of 12 x 12 yarns/25 mm. Thus woven, the victoria lawn was filled with polyvinyl alcohol size having a pH of 6.3 and a concentration of 10 % at 75°C, and then dried at 155°C.

[0083] The spun yarn was dissolved and hydrolyzed in an aqueous 1 N alkaline solution at 50°C for 15 minutes. Thus processed, the fibers constituting the yarn had voids formed inside them. As in the photograph of Fig. 2 that shows the cross sections of the fibers of the processed yarn, the outer skin (outer part) of each fiber remained as it was but the inside (inner part) thereof was corroded. Concretely, the single fibers in which the voids formed account for 55 % on average of the cross-sectional area of each fiber are about 90 % of the total number of the filaments.

[0084] The victoria lawn produced herein was buried in the ground. Before and after buried therein, the strength retentiveness of the yarn was measured. The weft of the sample was cut off, and the strength of the warp alone was measured.

[0085] Not processed with the fiber-processing agent mentioned below, the strength retentiveness of the sample was 96.9 % after 4 weeks. As opposed to this, the strength retentiveness of the sample that had been sprayed with 5 %, relative to the sample cloth, of a fiber-processing agent of a biodegradation promoter of a composition formulated by mixing a potassium stearyl phosphate, a polyether, an alkyl ether, a laurylamine and a nonionic surfactant in a ratio of 50:22:13:10:5, having a strength reduction-promoting constant (KR value) of 1.30 and having a pH of 9.5 was significantly reduced to 42.8 % after 4 weeks.

Example 2:

[0086] The non-stretched fibers prepared in the same manner as in Example 1 were bundled up into non-stretched tow of 456,000 dtex. The tow was then drawn in two stages. Concretely, the water bath temperature in the first drawing stage was 65°C, the water bath temperature in the second drawing stage was 95°C, the draw ratio in the first drawing stage was 3.30 times, the draw ratio in the second drawing stage was 1.15 times, and the total draw ratio was 3.80 times (88 % of the elongation at break). 0.3 % by weight of spinning oil ([KE3400] produced by TAKEMOTO OIL & FAT Co., LTD.) having a strength reduction-promoting constant (KR value) of 1.14 and having a pH of 7.2 was applied to the stretched tow, which was then crimped. For this, the forced crimper used has an inlet pressure of 3.0 kg/cm² and an outlet pressure of 2.5 kg/cm² and crimping rate was 80 m/min. Thus crimped, the number of buckles of the tow is 14 or 15/2.5 cm. The thus-crimped tow was cut with a cutter into 38-mm pieces, polylactic acid short fibers having a single fiber fineness of 1.7 dtex. The number of the cracks formed in the surfaces of the stretched short fibers was 9 per 10 cm of each single fiber, the specific gravity of the short fibers was 1.2381, the strength at break thereof was 2.9 cN/dtex, and the elongation at break thereof was 30.3 %. In point of their strength and elongation, the short fibers have no problem in practical use thereof.

[0087] The short fibers were spun in an ordinary manner into yarn of 10 tex.

[0088] The spun yarn was woven into victoria lawn of 12 × 12 yarns/25 mm. Thus woven, the victoria lawn was filled with polyvinyl alcohol size having a pH of 6.3 and a concentration of 10 % at 75°C, and then dried at 155°C.

[0089] The spun yarn was dissolved and hydrolyzed in an aqueous 1 N alkaline solution at 50°C for 15 minutes. Thus processed, the fibers constituting the yarn had voids formed inside them. As in the photograph of Fig. 2 that shows the cross sections of the fibers of the processed yarn, the outer skin (outer part) of each fiber remained as it was but the inside (inner part) thereof was corroded. Concretely, the single fibers in which the voids formed account for 65 % on average of the cross-sectional area of each fiber are about 93 % of the total number of the filaments.

[0090] The victoria lawn produced herein was buried in the ground. Before and after buried therein, the strength retentiveness of the yarn was measured. The weft of the sample was cut off, and the strength of the warp alone was measured.

[0091] Not processed with the fiber-processing agent mentioned below, the strength retentiveness of the sample was 94.4 % after 4 weeks. As opposed to this, the strength retentiveness of the sample that had been sprayed with 5 %, relative to the sample cloth, of a fiber-processing agent of a biodegradation promoter, oil ([TORICOL M75] produced by TAKEMOTO OIL & FAT Co., LTD.) having a strength reduction-promoting constant (KR value) of 1.25 was significantly reduced to 50.1 % after 4 weeks.

Example 3:

[0092] A polymer, poly-L-lactic acid of 6200 D grade (from Cargil-Dow LLC, having a number-average molecular weight of 74000 and an optical purity of 98.6 %) was spun into stretched polylactic acid fibers of 278 dtex/48 f. The spinning head temperature was 205°C, the first roller temperature was 50°C, the second roller temperature was 90°C, the third roller temperature was 90°C, the fourth roller temperature was 140°C, the cooling roller temperature was 50°C, the pre-stretching draw ratio was 1.01 times, the first stretching draw ratio was 1.73 times, the total draw ratio was 2.32 times (90 % of the elongation at break at room temperature), the winding up rate was 3565 m/min, and 0.8 % by weight of spinning oil ([KE3400] produced by TAKEMOTO OIL & FAT Co., LTD.) having a pH of 7.2 was applied to the polymer being spun into fibers. The elongation at break of the stretched fibers was 37.5 %.

[0093] Two-folded yarn of the stretched fibers was false-twisted, using a friction false-twisting machine. Concretely, the draw ratio was 1.05 times, the heater temperature was 140°C, D/Y was 756, and the yarn running speed was 200 m/min. Every single fiber of the false-twisted yarn had 25 cracks/10 cm, the strength of the yarn was 2.1 cN/dtex, and the elongation at break thereof was 28.7 %.

[0094] The thus-processed yarn was Z-twisted to a count of 300 twists/m. Using a rapier loom (produced by Tsudakoma Corp.), the thus-twisted yarn was woven into a plain weave fabric having an on-loom density of 63 × 45 yarns/

25 mm.

[0095] The fabric was then dyed as follows: This was scoured in hot water with no alkali therein at 80°C, dried, pre-set, dyed (in white), dried and then finally set. Thus processed, the final density of the fabric was 73 x 50 yarns/25 mm.

[0096] The processed yarn was dissolved and hydrolyzed in an aqueous 1 N alkaline solution at 50°C for 15 minutes. As a result, the fibers constituting the yarn had voids formed inside them. As in the photograph of Fig. 2 that shows the cross sections of the fibers of the processed yarn, the outer skin (outer part) of each fiber remained as it was but the inside (inner part) thereof was corroded. Concretely, the single fibers in which the voids formed account for 50 % on average of the cross-sectional area of each fiber are about 90 % of the total number of the filaments.

[0097] The fabric produced herein was buried in the ground. Before and after buried therein, the strength retentiveness of the yarn was measured. The fibers were carefully extracted out of the fabric, and their strength was measured.

[0098] Not processed with the alkaline fiber-processing agent mentioned below, the strength retentiveness of the sample was 89.2 % after 4 weeks. As opposed to this, the strength retentiveness of the sample that had been sprayed with 5 %, relative to the sample cloth, of an alkaline fiber-processing agent consisting essentially of potassium stearyl phosphate and having a pH of 9.5 was significantly reduced to 47.6 % after 4 weeks.

Comparative Example 1:

[0099] The non-stretched polylactic acid fibers prepared in Example 1 were bundled up into non-stretched tow of 372,000 dtex. The tow was stretched in two stages. Concretely, the water bath temperature in the first stage was 65°C, the water bath temperature in the second stage was 95°C, the draw ratio in the first stage was 2.50 times, the draw ratio in the second stage was 1.24 times, and the total draw ratio was 3.10 times (72 % of elongation at break). Next, 0.3 % by weight of finishing oil ([KE3400] produced by TAKEMOTO OIL & FAT Co., LTD.) having a strength reduction-promoting constant (KR value) of 1.14 and having a pH of 7.2 was applied to the stretched tow, which was then crimped. For this, the forced crimper used had an inlet pressure of 1.9 kg/cm² and an outlet pressure of 1.9 kg/cm². Thus crimped, the number of buckles of the tow was 14 or 15 per 2.5 cm. The thus-crimped tow was cut with a cutter into 38-mm pieces, polylactic acid short fibers having a single fiber fineness of 2.0 dtex. The number of the cracks formed in the surfaces of the stretched short fibers was 2 per 10 cm of each single fiber, the specific gravity of the short fibers was 1.2460, the strength at break thereof was 2.3 cN/dtex, and the elongation at break thereof was 52.3%.

[0100] The short fibers were spun in an ordinary manner into yarn of 10 tex.

[0101] The spun yarn was woven into victoria lawn of 12 x 12 yarns/25 mm, in the same manner as in Example 1. Thus woven, the victoria lawn was filled with polyvinyl alcohol size having a pH of 6.3 and a concentration of 10 % at 75°C, and then dried at 155°C, also in the same manner as in Example 1.

[0102] The spun yarn was dissolved and hydrolyzed in an aqueous 1 N alkaline solution at 50°C for 15 minutes. Thus processed, the fibers constituting the yarn had a few voids formed inside them. Concretely, the single fibers in which the voids formed account for about 3 % on average of the cross-sectional area of each fiber are about 50 % of the total number of the filaments, but the inside (inner part) of each fiber was not corroded.

[0103] The victoria lawn produced herein was buried in the ground. Before and after buried therein, the strength retentiveness of the yarn was measured. The weft of the sample was cut off, and the strength of the warp alone was measured.

[0104] Not processed with the fiber-processing agent mentioned below, the strength retentiveness of the sample was 105.8 % after 4 weeks. On the other hand, the strength retentiveness of the sample that had been sprayed with 5 %, relative to the sample cloth, of a fiber-processing agent of a biodegradation promoter of a composition formulated by mixing a potassium stearyl phosphate, a polyether, an alkyl ether, a laurylamine and a nonionic surfactant in a ratio of 50:22:13:10:5, having a strength reduction-promoting constant (KR value) of 1.30 and having a pH of 9.5 was still 80.2 % after 4 weeks.

Comparative Example 2:

[0105] Raw spun fibers prepared in the same manner as in Example 1 were bundled up into non-stretched tow of 120,000 dtex. The tow was stretched in two stages. Concretely, the water bath temperature in the first stage was 60°C, the water bath temperature in the second stage was 95°C, the draw ratio in the first stage was 3.60 times, the draw ratio in the second stage was 1.23 times, and the total draw ratio was 4.43 times (103 % of elongation at break). Next, 0.3 % by weight of spinning oil ([KE3400] produced by TAKEMOTO OIL & FAT Co., LTD.) having a strength reduction-promoting constant (KR value) of 1.14 and having a pH of 7.2 was applied to the stretched tow, which was then crimped. For this, the forced crimper used had an inlet pressure of 5.6 kg/cm² and an outlet pressure of 6.5 kg/cm². Thus crimped, the number of buckles of the tow was 14 or 15 per 2.5 cm. The thus-crimped tow was cut with a cutter into 38-mm pieces, polylactic acid short fibers having a single fiber fineness of 1.5 dtex. The number of the cracks formed in the surfaces of the stretched short fibers was 64 per 10 cm of each single fiber, the specific gravity of the short fibers

was 1.2109, and the strength at break thereof was 1.3 cN/dtex. The strength of the fibers is not enough for practical use.

Comparative Example 3:

- 5 [0106] Herein tried was spinning a polymer, poly-L-lactic acid having a number-average molecular weight of 47200 and an optical purity of 98.7 %, at a spinning head temperature of 200°C and a winding-up rate of 800 m/min. Though the polymer cobwebbed in some degree, its strength was too weak and it was impossible to wind up the polymer fibers.
- 10 [0107] As described in detail hereinabove with reference to its preferred embodiments, the present invention provides biodegradable fibers of which the physical properties are good and enough for ordinary daily use and of which the biodegradation can be controlled in any desired manner.

Claims

- 15 1. Biodegradable fibers of polylactic acid having a number-average molecular weight of from 50,000 to 150,000, which are characterized in that the alkali solubility of the inside part of each fiber is larger than that of the outer peripheral part thereof and the surface of each fiber has from 5 to 50 cracks/10 cm.
- 20 2. Biodegradable fibers as claimed in claim 1, to which is applied a fiber-processing agent having a pH of lower than 7.8.
3. Biodegradable fibers as claimed in claim 1, to which is applied a fiber-processing agent (a) whose strength reduction-promoting constant (KR value) represented by the following formula (1) is smaller than 1.2:

$$25 \quad \text{Strength Reduction-promoting Constant (KR value)} = TA/TB \quad (1)$$

wherein TA indicates the strength of the biodegradable fibers of claim 1, and the strength thereof is measured after the fibers are degreased and then left at a temperature of 50°C and a humidity of 65 % for 7 days; and

30 TB indicates the strength of the biodegradable fibers of claim 1, and the strength thereof is measured after the fibers are degreased, then from 1 to 5 % by weight of the fiber-processing agent (a) is applied to the fibers under a tension of from 0.05 to 0.20 g/dtex, and the thus-processed fibers are left at a temperature of 50°C and a humidity of 65 % for 7 days.

- 35 4. A fabric of the biodegradable fibers of any of claims 1 to 3.
5. A biodegradability-controlling method for promoting the biodegradation of the biodegradable fibers of claim 1 or 2, which comprises processing the surfaces of the fibers with an alkaline fiber-processing agent having a pH of not lower than 7.8.
- 40 6. A biodegradability-controlling method for promoting the biodegradation of the biodegradable fibers of claim 1, which comprises applying to the fibers a fiber-processing agent (b) of which the strength reduction-promoting constant (KR value) represented by the following formula (1) is not smaller than 1.2:

$$45 \quad \text{Strength Reduction-promoting Constant (KR value)} = TA/TB \quad (1)$$

wherein TA indicates the strength of the biodegradable fibers of claim 1, and the strength thereof is measured after the fibers are degreased and then left at a temperature of 50°C and a humidity of 65 % for 7 days; and

50 TB indicates the strength of the biodegradable fibers of claim 1, and the strength thereof is measured after the fibers are degreased, then from 1 to 5 % by weight of the fiber-processing agent (b) is applied to the fibers under a tension of from 0.05 to 0.20 g/dtex, and the thus-processed fibers are left at a temperature of 50°C and a humidity of 65 % for 7 days.

- 55 7. A biodegradability-controlling method for promoting the biodegradation of the biodegradable fibers of claim 1 or 2, which comprises applying to the fibers a fiber-processing agent that contains at least 1 % by weight of at least one component selected from a group consisting of organicphosphate salts, unsaturated fatty acids and unsaturated alcohols.

Figure 1



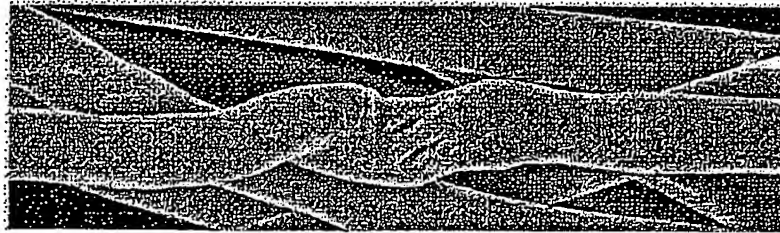
photograph substitute for drawing

Figure 2



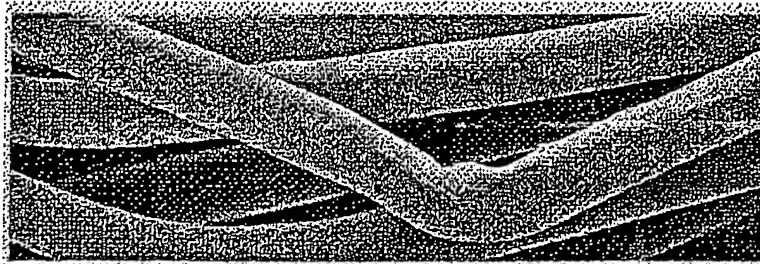
photograph substitute for drawing

Figure 3



photograph substitute for drawing

Figure 4



photograph substitute for drawing



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 02 5520

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 01, 31 January 2000 (2000-01-31) & JP 11 293519 A (UNITIKA LTD), 26 October 1999 (1999-10-26) * abstract *	1-7	D01F6/62 D06M13/144 D06M13/203 D06M15/53
A	--- PATENT ABSTRACTS OF JAPAN vol. 1997, no. 03, 31 March 1997 (1997-03-31) & JP 08 302526 A (UNITIKA LTD;CHIKYU KANKYO SANGYO GIJUTSU KENKYU KIKO), 19 November 1996 (1996-11-19) * abstract *	1-7	
P,A	--- YUAN X ET AL: "Comparative observation of accelerated degradation of poly(l-lactic acid) fibres in phosphate buffered saline and a dilute alkaline solution" POLYMER DEGRADATION AND STABILITY, BARKING, GB, vol. 75, no. 1, 2002, pages 45-53, XP004326574 ISSN: 0141-3910 * the whole document *	1-7	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			D01F D06M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 February 2003	Examiner Tarrida Torrell, J
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</p>			

EPO FORM 1503 03 02 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 02 02 5520

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-02-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 11293519	A	26-10-1999	NONE	
JP 08302526	A	19-11-1996	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)